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DIELECTRIC AND MECHANICAL PROPERTIES OF $\text{BaBi}_2(\text{Nb}_{0.99}\text{V}_{0.01})_2\text{O}_9$ CERAMICS

WŁASNOŚCI MECHANICZNE CERAMIKI BBN DOMIESZKOWANEJ WANADEM

The BBN ceramics doped by vanadium have been broadly recognized by using nano indentation techniques and ultrasound velocity and measurements. The results affirm that the vanadium admixture significantly improved the mechanical quality of ceramics. Such a small dopant doesn't change the dielectric properties, but we obtain visible increasing of the dielectric permittivity value and shifts the temperature of the ε_{max} to higher values. The vanadium admixture decreased the diffusion degree γ as well as influenced on the parameters characteristic for the relaxor behaviour. Our suggestion is that partial substitution of the smaller vanadium ions into the niobium sites renders for example ordering of the dipoles.

Keywords:

Własności mechaniczne ceramiki BBN domieszkowanej wanadem były szeroko badane przy użyciu zarówno techniki nanoindentacji, jak i pomiaru prędkości rozchodzenia się fal ultradźwiękowych w materiale. Otrzymane wyniki potwierdziły przypuszczenie, że domieszka wanadu znacznie poprawia własności mechaniczne ceramiki. Tak mała ilość domieszki nie wpływa w znaczący sposób na własności dielektryczne ceramiki, jednak wpływ ten jest zauważalny. Mianowicie wzrasta wartość maksymalna przenikalności dielektrycznej przy jednoczesnym przesunięciu odpowiadającej jej temperatury ku wyższym wartościom. Ponadto domieszka wanadu powoduje zmniejszenie stopnia rozmycia przejścia fazowego γ oraz wpływa na własności relaksorowe ceramiki.

1. Introduction

Ferroelectric materials with Bi-layered structure such as $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{SrBi}_2\text{Nb}_2\text{O}_9$ are now intensively investigated in view of their application in non-volatile computer memories and high temperature piezoelectric transducers. The most useful aspect of these materials are their high fatigue resistance against polarization switching. When Sr is replaced with Ba ions (BBN), structural disorder is induced and material exhibits significant broadening of the phase transition [1-4]. A wide range of applications required materials with not only good dielectric properties, but also high density, good mechanical quality and very well developed grain structure. Based on literature information the very promising to improve this features seems to be vanadium dopant [5,6]. In case of SBN ceramics the dopant remarkably improved not only the quality of ceramics, but also the dielectric properties. The main subject of this paper is the results of the ultrasound velocity measurements,

which allow us to determine the Young modulus and Poisson ratio. The comparison between these results with the other ones obtained by the nanoindentation techniques draw to very suprising conclusion. Namely the Young modulus in nano and macroscale differ markedly. The second part of paper is focused on dielectric properties of this interesting material. The pure BBN ceramics, as well as the modified ones by vanadium, show the frequency dependence of the dielectric response typical for relaxor ferroelectrics [7,8] i.e. the significant reduction of $\varepsilon\varepsilon'_{max}$ and shift of the corresponding temperature (T_m) towards higher values with the frequency increase.

2. Experimental conditions

$\text{BaBi}_2\text{Nb}_2\text{O}_9$ pure and doped by 1 at. % of vanadium ceramics were prepared by standard way using two-steps sintering process. Appropriate quantities of BaCO_3 , Bi_2O_3 , Nb_2O_5 were weighted and mixed. As

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the first step the conventional sintering at 950°C for 2h was carried out. Then the materials were crushed, milled and sieved and next pressed into the disk pallets for XRD and dielectric measurements and into a bar-shaped plate for mechanical ones. The second sintering was carried out at 1100°C for 6h in the case of undoped ceramics. The sintering temperature of vanadium content ceramics was lower and equal to 1050°C and the sintering process last 3h.

The grain structure and distribution of all elements throughout the grains were examined by scanning electron microscope, (SEM), JSM-5410 with an energy dispersion spectrometer (EDS), whereas the crystallographic structure and parameters of elementary cell were determined from XRD measurements carried out using Huber diffractometer. The powder diffraction diagram was measured from 10 to 100° in 2θ with 0.02° steps and a 2 s counting time and analyzed using a set of programs i.e. the DHN powder Diffraction System ver. 2.3.

Mechanical properties were verified by using three different methods, namely nanoindentation method and ultrasound measurements.

Nano-indentation experiments (TriboScope® nanoindenter, Hysitron Inc., Minneapolis, Minnesota) were carried out at room temperature in air using a Berkovich diamond tip with a 150 nm radius. The perfectness of the tip shape was verified on a fused quartz standard sample before and after measurements. The error was lower than the value of standard deviation. Load – displacement measurements were made under load-control with the maximum indentation force ranging between 10 and 1000 μ N. The loading and unloading rates were 10 μ N/s, with 15s pause at maximum force, 100 indents were performed for the sample.

The ultrasound velocities measurements were performed using the following equipment [9]:

- for longitudinal velocity an MT-571 (UNIPAN Company) with a pair of converters (0.5MHz) and device UZP-1 (INCO VERITAS),
- for transverse velocity a UZP-1 and converter with a frequency of 4MHz.

The dielectric measurements were carried out on heating in the temperature range 0-450°C using an HP4192A impedance analyser for the frequency of measuring field 0.1-1000 kHz.

3. Results

The preliminary investigations confirm our assumptions, vanadium admixture substantially improved the sinterability of BBN ceramics and caused insignificant increase of density from 7.07 up to 7.15 g/cm³. Vanadium admixture influenced also on grain structure of investigated ceramics. In Fig. 1 the typical scanning electro images are given for pure and 1 at. % content of vanadium ceramics. The average grain size decreased from 2.6 μ m to 2.9 μ m. The increase in grain size led to the decrease in grain boundary volume, which results in increase of density.

In order to check if the obtained ceramics show the structure characteristic for Aurivillius family and obtain the lattice parameter the XRD measurements were carried out on the ceramics samples at room temperature. The X-ray diffraction pattern (XRD) of BBN ceramics is shown in Fig. 2. The location and intensity of 32 diffraction lines were identified in the range of the measured angle. The obtained results show a good agreement with JCPDS standard number 12-0403 for BaBi₂Nb₂O₉. All line indexes connected with Aurivillius structure were

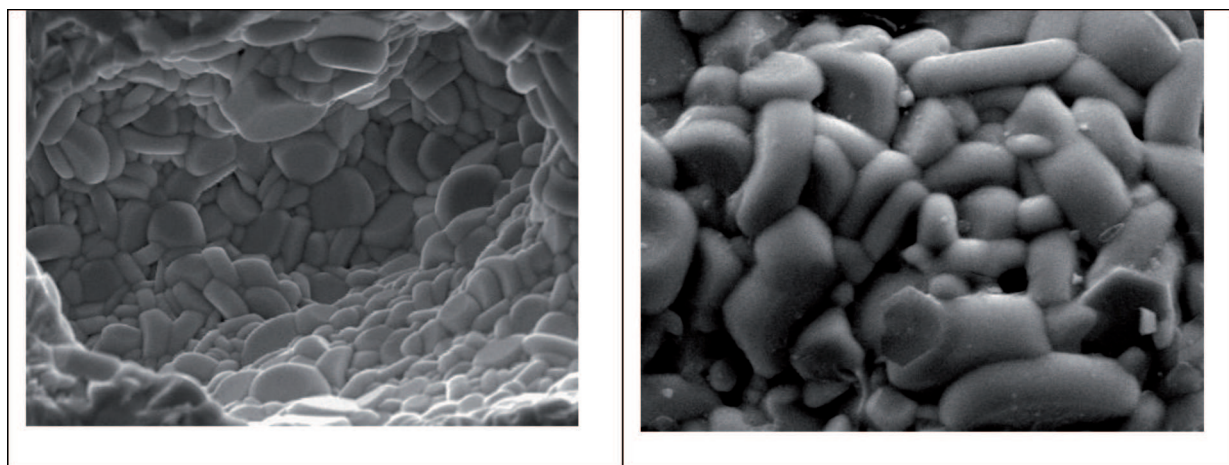


Fig. 1. SEM images of pure [2] and doped BaBi₂Nb₂O₉ ceramics

assigned for all investigated ceramics. For pure ceramics, as was mentioned in our previous paper [2], the presence of a single very weak line for $2\theta=25.58^\circ$ not connected with the Aurivillius structure was perceived. This line is probably connected with the strongest diffraction line of BaCO_3 structure (JCPDS standard No. 11-0697), which confirmed our opinion about presence of a small quantity of BaCO_3 . The ratio of the integral intensity of this line to the integral intensity of all the lines of diffraction pattern allowed estimate the content of the BaCO_3 phase at ca 0.5%. In case of vanadium dopand BBN ceramics measurements revealed that the single phase layered perovskites was formed without any detectable secondary phase, which confirm that the admixture truly improve sinterability of ceramics. The pure BBN ceramics as well as vanadium doped were characterized by tetragonal structure with space group $I4/mmm$ [10,11].

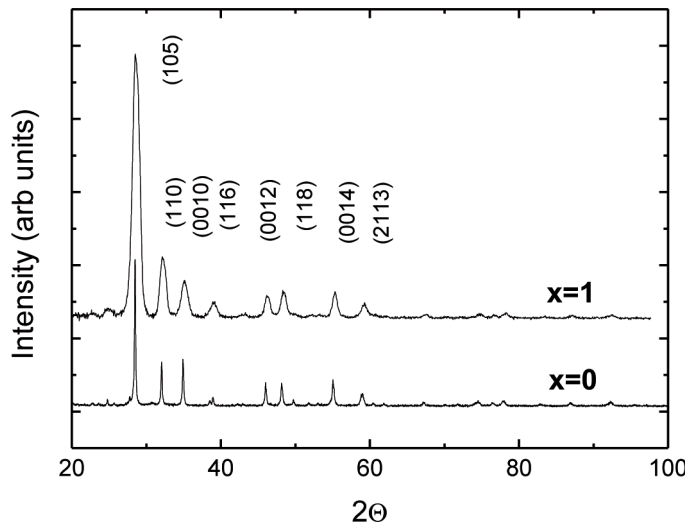


Fig. 2. XRD pattern of BBN ceramics of pure and doped $\text{BaBi}_2\text{Nb}_2\text{O}_9$ ceramics

Additionally the XRD measurements allow to determine the lattice parameter, which are insignificantly smaller for doped ceramics. For comparison, in case of pure ceramics the lattice parameters are equal to $a=b=3.944\text{\AA}$, and $c=25.63\text{\AA}$ (these results are in a good agreement with the results reported in [12]), whereas for

vanadium modified ceramics the parameter was equal to $a=b=3.943$ and $c=25.60$ decreased, as it was expected. However the decrease is not such significant, as it results from comparing the value of vanadium and niobium radii. It is connected with specific shape of layered structure perovskites. Namely the crystal structure may not change to a larger extent unlike in case of nanolayered perovskites with doping, because of the structural constraint imposed by $[\text{Bi}_2\text{O}_2]^{2+}$ interlayer [13].

As was mentioned above the mechanical quality of samples is very important from the point of view of their further applications. It was reason to undertake the mechanical research of obtained samples in macro and nanoscale by using two different methods. The first was nanoindentation. The measurements were made by using TriboScope[®] nanoindenter produced by Hysitron Inc., Minneapolis, Minnesota. The procedure of measuring was described above. The surface image of the BBN sample used for test and trace of the Berkovich tip nanoindentation marked on it is shown in Fig. 3a. The load-displacement (tip penetration depth) curves as a function of indentation load during nanoindentation for BBN specimen is shown in Fig. 3b. These load displacement curves were used to extract the values mechanical parameters of the BBN samples. Values of hardness H and elastic modulus E_r obtained for the discussed ceramics is given at Table 1. Young's modulus (E) of the specimen can be extracted according to the following formula:

$$\frac{1}{E_r} = \left(\frac{1 - \mu^2}{E} \right)_i + \left(\frac{1 - \mu^2}{E} \right)_s \quad (1)$$

The subscript i indicates a property of the indenter material, namely the value of Young's modulus and Poisson's ratio. For the diamond Berkovich tip used, E_i and μ_i are equal to 1140 GPa and 0.07 [14], respectively. The subscript s indicates the same property of the specimen. For determination of E_s value the Poisson's ratio μ_s should be known. The value in question was obtained based on measurements of ultrasound velocities. Young modulus calculated based on results obtained from nanoindentation technique and relationship (1) are given at Table 1.

TABLE 1

BBN ceramics	Nanoindentation measurements			Ultrasound velocity measurements			
	H [GPa]	E_r [GPa]	E [GPa]	V_L [m/s]	V_T [m/s]	μ	E [GPa]
Pure	9.19	106	107.7	3647.7	2187.5	0.219	76.06
1 at. % doped	10.80	159	168.19	4119.1	2489.7	0.212	91.7

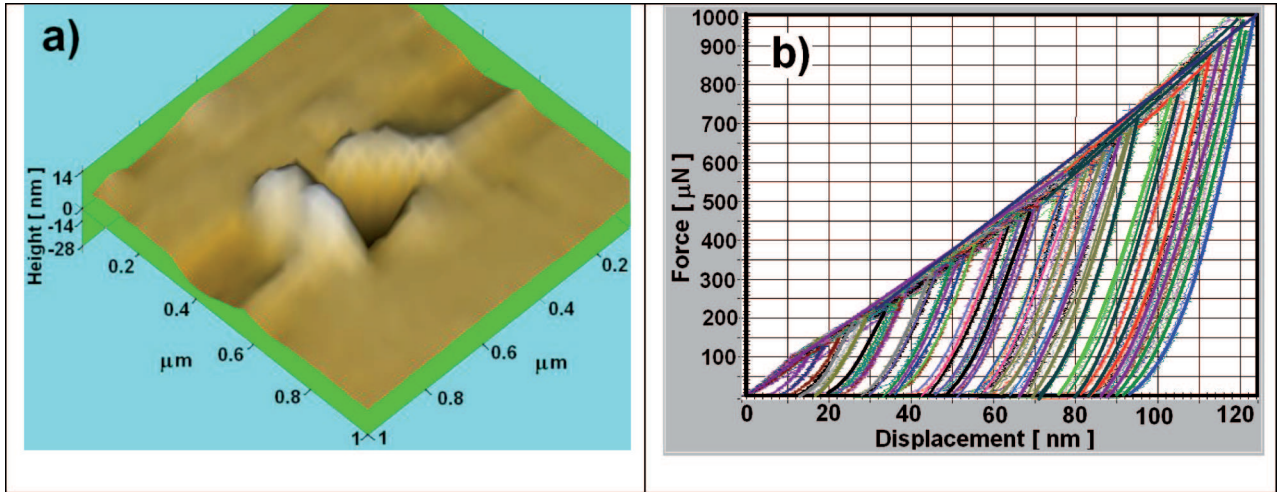


Fig. 3. The AFM microscope image of the examined sample surface (a) the load-displacement curves for nanoindentation test (b) obtained for 1 at.% of vanadium dopant

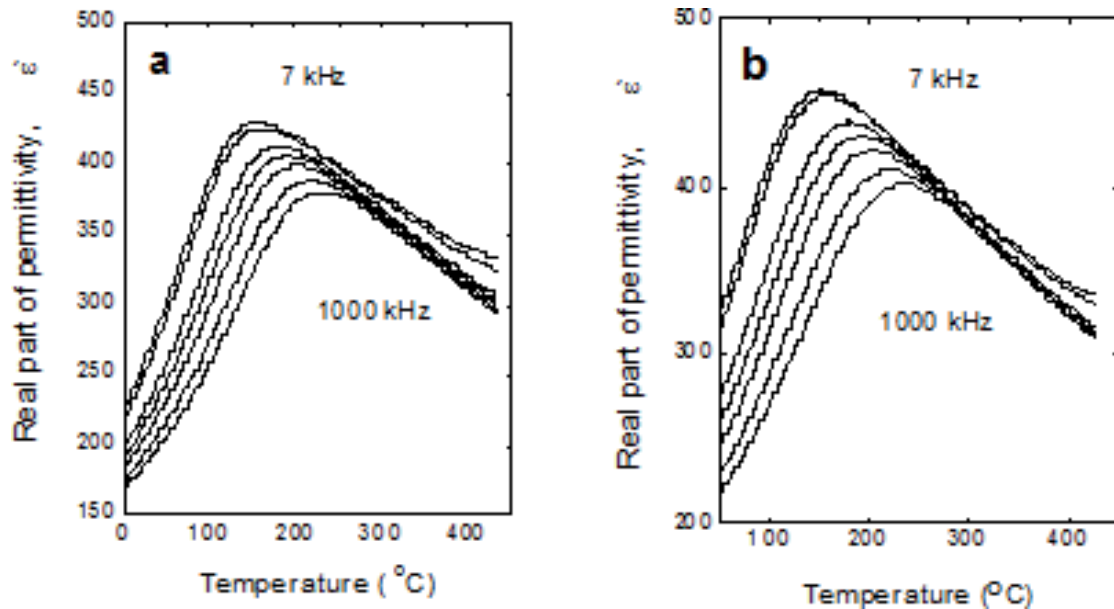


Fig. 4. Real part of permittivity as a function of temperature measured on heating at frequency of measuring field 100kHz for pure and doped BaBi₂Nb₂O₉ ceramics

As was mentioned above the second technique used to investigate the mechanical properties of BBN ceramics was measurements of ultrasound velocity. The velocity of the longitudinal V_L and the transverse V_T waves in pure and doped BBN sample were measured and the results are given at Table 1. Based on the following formulas [9]:

$$\mu = \frac{V_L^2 - 2V_T^2}{2(V_L^2 - V_T^2)} \quad (2)$$

and

$$E = \frac{V_L^2 \rho (1 + \mu)(1 - 2\mu)}{(1 - \mu)} \quad (3)$$

where ρ – density of the specimen the Poisson's ratio μ and Young's modulus E were calculated. The results of calculations are presented at Table 1.

Comparison value of Young's modulus obtained by ultrasound velocities measurements and nanoindentation method different significantly from each other. It could be explained in the following manner: The results obtained from measurements of internal friction and ul-

trasound velocities "feel" the macroscopic response of spatially inhomogeneous state with interfaces and grain boundaries, which may be very mobile. The nanoindenter "feel" the local response of the single grain, which may be closer in value to the response of spatially homogeneous state. The comparison of results for doped and pure ceramics on nanoscale as well as macroscale allow to draw the following conclusion: the vanadium additives improved the mechanical quality of samples. This results stay with good correlation with the dielectric ones. Fig.4 shows the temperature characteristic of dielectric permittivity for a number of frequency of measuring field for undoped and vanadium content ceramics. Both ceramics show the relaxor behaviour with the characteristic frequency dispersion of T_m . However the degree of this dispersion (defined as the difference between T_m measured at 0.7 and 1000 kHz) insignificantly decreased from 92.5°C to 89°C. Additionally vanadium dopand caused the increase the maximal value of dielectric permittivity and shift of temperature T_m , corresponding to the broadened maximum in $\epsilon(T)$ curve to high values. The diffuseness in the phase transition has been studied as a function of vanadium content by estimating the degree of diffuseness γ using the following relation:

$$\frac{1}{\epsilon'} - \frac{1}{\epsilon'_{\max}} = \frac{C}{(T - T_{\max})^\gamma} \quad (4)$$

where ϵ_{\max} is the maximum value of the dielectric constant at the transition temperature (T_m), C the Curie-like constant and γ is the degree of diffuseness. The limiting values 1 and 2 for γ , respectively, reduce the expression to the Curie-Weiss law valid for a normal and the quadratic dependence valid for the ideal relaxor ferroelectric. The value of γ factor gradual decrease with increasing from 1.45 for undoped BBN up to 1.4 for 1 at.% vanadium doped BBN ceramics. The decrease in the value of γ implies that there is a decrease in the diffuseness of the transition. It is concluded from this observation that the partial incorporation of smaller vanadium ions on the niobium sites renders ordering of dipoles [5]. The attempts of determination the freezing temperature and energy of polarization fluctuations from Vogel-Fulcher relationship were undertaken. The relationship is presented below:

$$f = f_0 \exp \left[\frac{-E_a}{k(T_m - T_f)} \right]$$

where E_a is the activation energy, T_f is the freezing temperature of polarization fluctuations, and f_0 is the pre-exponential factor. The activation energy and freezing temperature of both pure and undoped samples are following: pure BBN ceramics $E_a=0.46\text{eV}$ $T_f=170\text{K}$,

1 at. % doped ceramics $E_a=0.41\text{eV}$ $T_f=195\text{K}$. The freezing temperature T_f shifts to high values. The comparison of this value with the values of T_m allows to suppose the temperature range of relaxor properties becomes insignificantly narrowed.

4. Conclusions

The presented above results prove that the vanadium admixture significantly improved the mechanical quality of ceramics. The influence of this dopant on dielectric properties is not so strong as in case of the mechanical properties. The vanadium content causes small increase of dielectric permittivity value and shifts the temperature corresponding to the ϵ_{\max} to higher values. Additionally the measurements revealed that the vanadium admixture decreased the diffusion degree γ as well as influenced on the parameters characteristic for the relaxor behaviour. The mentioned facts allow to conclude, that partial incorporation of smaller vanadium ions on the niobium sites renders ordering of dipoles, which was also previously suggested by [4].

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